PATENT SPECIFICATION (11) 1442885

(21) Application No. 43002/74 (22) Filed 3 Oct. 1974
(31) Convention Application No. 2350295 (32) Filed 6 Oct. 1973 in
(33) Germany (DT)
(44) Complete Specification published 14 July 1976
(51) INT CL² C11D 10/02//(C11D 10/02 1/72 3/04 3/075 3/08 3/12 3/395)
(52) Index at acceptance
C5D 6A4B 6A5B 6A5C 6A5D1 6A5D2 6A5E 6A5F 6A6 6A7 6A9 6B12M 6B12N1 6B12N2 6B3 6B6 6B9 6C6
D1P 1A1A5 1A1A7 1A1A8 1A5

(72) Inventor HELMUT HARTENSTEIN

(54) CHLORINE STABLE DETERGENTS

(71) We, JOH. A. BENCKISER GMBH, of 6700 Ludwigshafen/Rhein, Postfach 21 0167 Germany, a German Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to detergent compositions, especially to alkaline hydrous detergents which are suitable for dishwashing containing active chlorine releasing compounds.

Alkaline detergent compositions which comprise basically a builder, an alkali metal silicate and a low lather non-ionic surface active agent are generally used for cleaning dishes in dish washers. To improve the cleaning effect of such compositions, more particularly to remove stains such as tea stains, coffee stains, fruit juice residue etc., bleaching agents are added to the compositions which agents release oxygen or, preferably, chlorine in aqueous solution.

These known detergents containing active chlorine releasing compounds all have the disadvantage that the available chlorine content decreases during storage and thus the cleaning effect is reduced. This becomes more apparent the more water there is in the detergent compositions, which water may be the water of crystallization of the raw materials and/or may be added or formed when preparing the compositions, e.g. through the granulating process. Only those mixtures which are prepared from completely anhydrous raw materials remain sufficiently stable on storage.

However, a certain amount of water in the raw materials is essential in order to provide a rapidly dissolving product which can be satisfactorily and completely rinsed out from the dosing or measuring devices in the dish-washer and this again leads to the rapid decomposition of the chlorine releasing components.

It has now been found that a stable, active chlorine releasing compound-containing alkaline detergent compositions can be obtained if a chlorine stabilizer comprising a mixture of aluminium salt and zinc salt, in a weight ratio of 1:10—10:1 calculated as aluminium oxide and zinc oxide, is added to the composition.

According to the invention, therefore, there is provided a detergent composition in the form of a powder or granules containing an active chlorine releasing-compound and, as stabilizer, a mixture of an aluminium salt and a zinc salt in a weight ratio of 1:10—10:1 calculated as aluminium oxide and zinc oxide.

The stabilizer content is suitably from 0.05 to 5% by weight, preferably about 0.4% by weight, calculated as aluminium oxide and zinc oxide.

Suitable aluminium salts for use in the compositions of the invention include aluminium sulphate, aluminium chloride, alkali metal aluminates and water-insoluble aluminium compounds such as basic aluminium phosphate, aluminium stearate, aluminium silicate or even double salts such as alkali metal aluminium silicates, alkali metal aluminium phosphates and alkaline earth metal aluminium silicates.

Suitable zinc salts for use in the compositions of the invention include zinc sulphate, zinc chloride, alkali metal zincates or insoluble zinc compounds such as zinc stearate, zinc silicate and zinc phosphate.

Double compounds of zinc and aluminium can also be used, for example zinc-aluminium silicate, zinc-aluminate (e.g.

$$Zn[Al(OH)_4]_2)$$

and aluminium zincate (e.g.

$$Al_2[Zn(OH)_4]_3)$$

Examples of active chlorine releasing compounds which may be used in the compositions of the invention include sodium and potassium salts of di- and trichloroisocyanuric acids, sodium, calcium and lithium salts of hypochlorous acid, chlorinated trisodium orthophosphate, trichloromelamine, N-chloro-

acetyl urea and chloramine. They are suitably present in the composition to give an available chlorine level of from 0.5 to 5 percent, preferably about 1 percent.

In addition to the chlorine stabilizer and the active chlorine releasing compounds, the compositions according to the invention may also contain the conventional ingredients present in dish-washer detergent compositions. However, a particular advantage is that in accordance with the invention, the raw materials need not be in the anhydrous state but it is possible to use raw materials containing water of crystallization without the water content causing a loss of available chlorine during storage.

An important ingredient of the compositions is thus a sequesterant builder, preferably an alkaline reacting tripolyphosphate which suitably forms from 20 to 80 percent, preferably from 30 to 60 percent by weight, of the composition. In a product which can be easily rinsed out the water content should be from 3 to 15 percent, preferably from 4 to 8 percent by weight. Thus, the fully hydrated tripolyphosphate may be used as the hexahydrate. Other builders such as phosphonates or nitrogen-containing organic sequestering agents such as nitrilotriacetic acid or ethylene diamine tetracetic acid or nitrogen-free organic sequestering agents such as polycarboxylic acids may be present in the compositions.

Furthermore, the detergents may contain silicates, preferably sodium silicate. The ratio of Na_2O to SiO_2 is suitably in the range from 1:1 to 1:3.5. Volumes of 5—79 percent, preferably 20—50 percent, based on the mixture are used. In order to prevent discolouration and smearing, the water content of the silicate may be from 1 to 10 percent, preferably about 5 percent. However, the pentahydrate with about 42 percent of water may also be used.

It is also generally important that a certain relationship is maintained between SiO_2 and P_2O_5 since on the one hand the cleaning effect is at its best owing to the synergistic effects and on the other corrosion is reduced to a minimum. The ratio $P_2O_5 : SiO_2$ should preferably be from 1:0.7 and 1:2, most preferably about 1:1.

The non-ionic surface-active agents are preferably low lather agents such as low ethoxylated (e.g. containing 3—20 moles ethylene oxide) nonylphenolpolyglycolether, polypropylene-polyethylene-block polymerisation products and fatty alcohol ethoxylates of C_9—C_{18} fatty alcohols with 3—6 moles of ethylene oxide. Finally, the mixtures may also contain other conventional ingredients such as dyes and perfumes.

The preparation of the compositions according to the invention is carried out using convention methods such as mixing or granulation. They are used in the solid form in the standard concentrations.

The detergents according to the invention can be stored for a long time without there being any significant loss of available chlorine and thus cleaning effect. Owing to their water content, the detergents are readily soluble and can be easily and completely rinsed out of the dosing or metering devices of dish-washers.

A satisfactory stabilizing effect is only achieved with using mixture of aluminium salts and zinc salts in accordance with the invention and aluminium salts alone and zinc salts alone do not have any chlorine stabilizing effect.

Detergent compositions of the following formulations (not containing any stabilizer) were examined for chlorine stability. For this purpose the detergents were stored at 40°C and the available chlorine content determined at different time intervals. In the formulations all percentages are by weight.

Comparative Example I
50% sodium phosphate, anhydrous
40% sodium metasilicate, anhydrous
2% potassium dichloroisocyanurate
2% polypropylene - polyoxyethylene block polymerization product
6% sodium carbonate, calc.

Comparative Example II
50% sodium tripolyphosphate with 5% water
40% sodium metasilicate with 3% water
6% soda
2% fatty alcohol ethyoxylate C_9—C_{11} with 3 moles ethylene oxide
2% potassium dichloroisocyanurate

Comparative Example III
36% sodium tripolyphosphate with 3% water
60% sodium metasilicate with 5 moles water (contains 42% water)
2% nonylphenolethoxylate with 5 moles ethylene oxide
2% potassium dichloroisocyanurate

Evaluation of the chlorine stability at 40° gave the following results:

TABLE 1

Comparative Example	I	II	III
Initial available chlorine content	1.2	1.2	1.2
after 1 month	1.1	1.0	1.0
after 3 months	0.8	0.7	0.6
after 6 months	0.7	0.4	0.3
Rinsability	poor	good	good

These results show the relatively rapid reduction in available chlorine content and thus the drop in the cleaning efficiency, particularly with regard to stains such as tea stains, coffee stains and fruit juice residues. The effect is particularly clear in receptacles which contain

water. However, on the other hand, the hydrous products can be easily rinsed out.

The following detergent compositions containing zinc and aluminium salts as stabilizer and also containing zinc on aluminium salts alone were made up.

Example IV

A detergent of the following composition:
50% sodium tripolyphosphate with 5% water
40% sodium metasilicate with 3% water
2% sodium carbonate
2% fatty alcohol ethoxylate C_9—C_{11} with 3 moles ethylene oxide
2% potassium dichloroisocyanurate was mixed with:
a) 4% aluminium zinc silicate with 5% aluminium oxide and 8% zinc oxide, corresponding to 0.2% aluminium oxide+ 0.32% zinc oxide (according to the invention)

(Comparative)
b) 2.6% zinc silicate, corresponding to 0.53% zinc oxide;

(Comparative)
c) 3.3% aluminium silicate, corresponding to 0.53% aluminium oxide; and

(Comparative)
d) 1.25% aluminium silicate, corresponding to 0.2% aluminium oxide+ 0.32% B_2O_3; respectively and made up to 100% with Na_2SO_4.

Example V

33% sodium tripolyphosphate with 3% water
58.6% sodium metasilicate with 5 moles water (contains 42% water)
2% nonylphenolethoxylate with 5 moles ethylene oxide
2% potassium dichloroisocyanurate
4% calcium-aluminium-silicate, corresponding to 0.2% aluminium oxide
0.4% zinc phosphate, corresponding to 0.2% zinc oxide.

Example VI

60% sodium tripolyphosphate with 5% water
30.5% sodium metasilicate with 5 moles water (contains 42% water)
2% nonylphenolethoxylate with 4 moles ethylene oxide
2% potassium dichloroisocyanurate
5.5% aluminium-zinc-silicate, corresponding to 0.2% aluminium oxide and 0.6% zinc oxide.

The aluminium-zinc-silicate was prepared in the following way:

A solution (A) comprising 680 g waterglass with 9.6% Na_2O+24.8% SiO_2 was diluted to 2 litres of water.

A solution (B), comprising 50.3 g aluminium sulphate and 47.7 g zinc sulphate, was likewise diluted to 2 litres of water.

Both solutions were slowly poured in at the same time at a pH value of 7—8 in 2 litres water at 80° and maintained at this temperature. After these solutions had been completely mixed, the precipitate was drawn off, washed free of sulphate and dried at 130°. The pulverized substance had the following composition:

3.6% aluminium oxide
10.8% zinc oxide
5.7% Na_2O
69.0% SiO_2
remainder water.

5.5% of the substance prepared was used, corresponding to 0.2% aluminium oxide and 0.6% zinc oxide.

Example VII

Ratio Al_2O_3 : ZnO = 1 : 10
40% sodium tripolyphosphate with 5% water
53.31% sodium metasilicate with 5 moles water
2% nonylphenolpolyglycolether with 3 moles ethylene oxide
2% potassium dichloroisocyanurate
0.69% aluminium sulphate with 29% Al_2O_3, corresponding to 0.2% Al_2O_3
2.0% ZnO

Example VIII

60% sodium tripolyphosphate with 7% water
30.84% sodium metasilicate with 5 moles of water
2% C_{16}—C_{18} fatty alcohol ethoxylate with 6 moles ethylene oxide
2% potassium dichloroisocyanurate
0.40% Zn-sulphate with 50.3% ZnO, corresponding to 0.2% ZnO.
4.76% Al-phosphate with 42% Al_2O_3, corresponding to 2% Al_2O_3

Evaluation of the chlorine stability of the above compositions when stored at 40°C gave the following results:

TABLE 2

Example	Initial available chlorine content	1 month	3 months	6 months
IV a)	1.2	1.0	1.0	0.9
IV b)	1.2	1.0	0.65	0.4
IV c)	1.2	1.0	0.6	0.3
IV d)	1.2	1.0	0.7	0.5
V	1.2	1.1	1.0	0.9
VI	1.2	1.1	1.0	1.0
VII	1.2	1.1	1.0	0.9
VIII	1.2	1.15	1.1	1.0

These comparison tests clearly show the excellent chlorine stability of the detergent compositions according to the invention compared to detergent compositions of the same composition but not containing any chlorine stabilizer or only containing Al to Zn salts. The products according to the invention can be easily and entirely washed out from dosing or metering devices.

WHAT WE CLAIM IS:—

1. An alkaline detergent composition in the form of a powder or granules containing an active chlorine releasing-compound and, as stabilizer, a mixture of an aluminium salt and a zinc salt in a weight ratio of 1:10—10:1 calculated as aluminium oxide and zinc oxide.

2. A composition as claimed in Claim 1 containing from 0.05 to 5.0 percent by weight of stabilizer, calculated as aluminium oxide and zinc oxide.

3. A composition as claimed in Claim 1 or Claim 2 containing a zinc aluminium double salt as chlorine stabilizer.

4. A composition as claimed in Claim 3 in which the stabilizer is zinc aluminium silicate.

5. A composition as claimed in any one of the preceding claims containing from 0.5 to 5.0 percent by weight of active chlorine releasing compound.

6. A composition as claimed in any one of the preceding claims comprising a sequestrant builder, an alkali metal silicate and a non-ionic surface active agent.

7. A composition as claimed in Claim 6 in which the sequestrant builder is an alkaline reacting tripolyphosphate.

8. A composition as claimed in Claim 7 in which the phosphate is present in an amount of from 20 to 80 percent by weight of the composition.

9. A composition as claimed in Claim 8 in which the phosphate is present in an amount of from 30 to 60 percent by weight of the composition.

10. A composition as claimed in Claim 13 Claims 6—9 in which the silicate is a sodium silicate having an Na_2: SiO_2 ratio of from 1:1 to 1:3.5.

11. A composition as claimed in Claim 10 containing a phosphate builder in which the ratio P_2O_5: SiO_2 is from 1:0.7 to 1:2.

12. A composition as claimed in Claim 11 in which the said ratio is about 1:1.

13. A composition as claimed in any one of Claims 6—12 containing from 5 to 79 percent by weight of alkali metal silicate.

14. A composition as claimed in Claim 13 containing from 20 to 50 percent by weight of alkali metal silicate.

15. A composition as claimed in Claim 1 substantially as hereinbefore described with reference to the Examples.

MARKS & CLERK,
Chartered Patent Agents,
57—60, Lincolns Inn Fields,
London, WC2A 3LS,
Agents for the Applicant(s).

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.